Synchrotron XRD, XRF, and XANES studies of Jurassic Fish Coprolites

A. Lanzirotti (Univ. of Chicago), M. Becker (SUNY Stony Brook), G. Hanson (SUNY Stony Brook), and S. Sutton (Univ. of Chicago)

Abstract No. lanz1287
Beamline(s): **X26A**

Introduction: The Shuttle Meadow Formation is the lowermost Jurassic sedimentary unit of the Hartford Basin in southern Connecticut. Although siliciclastic alluvial sediments dominate the formation it contains a single black shale horizon that is believed to represent the deposition of sediment in an offshore environment. This black shale contains abundant, fully articulated fish fossils (genus *Semionotus, Redfieldius, Diplurus*) and their associated coprolites (fossilized fecal material). Interestingly, many of these coprolites, now preserved as phosphatic material, have very high levels of uranium (up to 600 ppm). In this study the X26A microprobe beamline was used to try and evaluate the reasons why such coprolites are so enriched in uranium, which has general implications for our understanding of the mobility and speciation of uranium in sediments. The microfocussing capabilities of the beamline were used to evaluate the variability in mineralogy (XRD), chemistry (XRF), and uranium speciation (XANES) in these sediments all at 10μm spatial resolution on thin-section samples.

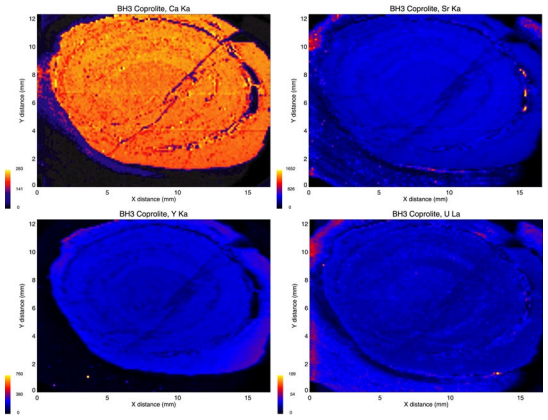

Figure 1. XRF compositional map of a ca. 12 mm x 17 mm cross-section through a coprolite. Maps show distribution in normalized fluorescence counts for Ca Ka (upper left), Sr Ka (upper right), Y Ka (lower left), and U La (lower right).

Methods and Materials: Analyses were conducted on 300 μm polished thin-sections of coprolite mounted on glass with epoxy. The incident beam was tuned to the U L3 binding energy using our Si(111) channel cut monochromator. This 350 μm collimated monochromatic beam was then focused to 10 μm in diameter using our system of Rh coated Kirckpatrick-Baez mirrors. XRF compositional data and fluorescence mode XANES were collected using a Canberra SL30165 Si(Li) detector. XRD data were collected using a Brucker SMART CCD system in reflection mode geometry.

Results: X-ray microdiffraction shows that these samples are dominated by three mineralogic components. Dolomite is the dominant mineral in the fine-grained matrix that hosts the coprolites, fluorapatite is the principal component of the coprolite itself, and pyrite can be found throughout the sample but primarily localized along late fractures in the host rock. The dolomite and fluorapatite both yield good powder diffraction patterns at 10 μm resolution, suggesting most of this material is microcrystalline. Although dolomite is the primary phase in the matrix and apatite in the coprolite, micro-XRD shows that some fine-grained components of each occur throughout the section. In thin-section these coprolites display pronounced optical zoning. The XRD suggests there is little mineralogic variability that defines this zoning, but it most likely reflects differences in grain size and/or abundance of organic carbon. Interestingly, the XRF compositional mapping shows that major and trace elements in these coprolites track the optical zoning (Figure 1). The major element Ca (2+) and the trace elements Sr (2+) and Y (3+), elements that are known to readily substitute for each other, show similar compositional zoning. U however displays a zoning profile inverse to that shown by the 2+ and 3+ cations. Additionally, XANES analyses of the U in these coprolites shows that although there is some variability in the speciation of U in these samples, the XANES spectra are most consistent with the U being in 6+ form.

Conclusions: 'Black shales' such as the one analyzed here are generally thought to have been deposited in dysoxic to anoxic, depleted bottom waters. Coprolites are believed to provide a nucleation site for HPO_4^-, resulting in the precipitation of phosphate. This phosphatization is believed to begin before the complete decay of the organic material. Earlier fission track mapping of these samples confirmed the high abundance of uranium but lacked the spatial resolution needed to identify the patterns of U distribution or its mineralogic and trace element correlations. The XRF compositional mapping at X26A showing that the uranium is inversely correlated with 2+ and 3+ cations and the preliminary XANES spectroscopy showing that much of the U may be in an oxidized form calls into question many of the assumptions regarding the reducing conditions under which such sediments are deposited and the role of organic matter in localizing U in sediments.

Acknowledgments: This research was funded by grant DOEFG0292ER14244 to S. Sutton and DERO294ER14449 to G. Hanson and W. Meyers.